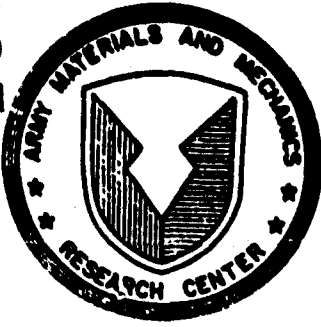AD

AMMRC CTR 72-4

DEVELOPMENT OF POLYCRYSTALLINE SPINEL FOR TRANSPARENT ARMOR APPLICATIONS
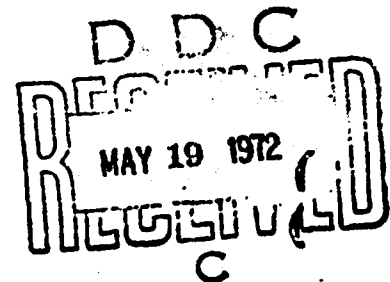
March 1972

HAYNE PALMOUR III
ENGINEERING RESEARCH SERVICES DIVISION
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RALEIGH, NORTH CAROLINA 27607

FINAL REPORT   CONTRACT NUMBER DAAG 46-69-C-0097

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MAY 19 1972

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Prepared for

ARMY MATERIALS AND MECHANICS RESEARCH CENTER
Watertown, Massachusetts 02172

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13. ABSTRACT

This study was undertaken to determine the feasibility of producing substantial quantities of pure, undoped $MgAl_2O_4$ spinel powder from a chemical precursor in a semicontinuous process, and thereafter, of densifying the powder by hot molding and/or rate controlled sintering processes on a best efforts basis to achieve optical transparency in this isotropic material. The precursor salt was a mixed magnesium aluminum sulphate hydrate produced on a batch basis by direct melting of the starting salts and subsequent solidification by cocrystallization. Partially dehydrated precursor was dynamically precalcined at ~650°C, and then dynamically calcined at ~1150°C in an inclined rotating tube furnace. The overall powder production process was not properly regulated (for reasons almost unrelated to its basic technology), resulting in poor chemical control of cation stoichiometry and incomplete removal of sulphur residues during calcination. Consequently specimens hot molded from gas-laden, non-stoichiometric powder displayed poorer optical properties than had been occasionally obtained in prior work. Rate controlled sintering studies produced well documented evidence of non-Arrhenian densification kinetics for (nonisothermal) linear controlled-rate densification over the range 60-90% fractional density. These findings, indicative of plastic flow as the dominant transport mechanism, are considered to be pertinent to successful densification of spinel by both simple and stress-augmented sintering (hot pressing or hot molding).

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Lightweight armor						
Transparent armor						
Spinel						
Hot pressing						
Powder (particles)						
Physical properties						
Sintering						
Calcining						

AMMRC CTR 72-4

DEVELOPMENT OF POLYCRYSTALLINE SPINEL FOR TRANSPARENT ARMOR APPLICATIONS

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FOREWORD

This report was prepared by the Department of Engineering Research at North Carolina State University under U. S. Army Contract DAAG-46-69-C-0097. The work was administered under the direction of Capt. D. T. Rankin and Mr. G. E. Gazza.

This report covers the period 16 June 1969 through 31 January 1970, and includes certain follow-up activities which extended through calendar year 1970. University personnel participating in this study included H. Palmour III, W. W. Kriegel, K. O. Beatty, D. R. Johnson, V. A. Dixon, C. E. Zimmer, J. F. Freeman, N. M. Shah, C. Batts, T. Miller, R. E. Haggas, V. Daniel, and M. V. Karia. Helpful assistance by P. F. Becher, M. L. Huckabee, C. H. Kim, E. M. Gregory, E. B. Roberts, W. B. Wilson, T. Banther, and J. P. Kirkland in experimental activities, preparation and analysis, and by Mrs. Ann Ethridge, Miss Anne Young and M. L. Huckabee in report preparation, is gratefully acknowledged.

Finally, it is appropriate to acknowledge helpful discussions with R. Clark and R. J. Weagley (Eastman Kodak Company), J. L. Pentecost, N. Levy, Jr., and D. D. Walczyk (W. R. Grace & Company), W. H. Rhodes (AVCO Corp.), and D. Roy, F. Stermole, D. G. Wirth and D. Sellers (Coors Porcelain Co.).

This project has been accomplished as part of the U. S. Army Manufacturing Methods and Technology Program, which has as its objective the timely establishment of manufacturing processes, techniques or equipment to insure the efficient production of current or future defense programs.

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INTRODUCTION

As early as 1961-62, the possibilities of achieving transparency in polycrystalline isotropic spinel ceramics were considered and occasionally even demonstrated (in portions of small hot pressed specimens) in research studies at North Carolina State University concerned primarily with the structural and mechanical properties of spinel ceramics.[1-3] Novel methods for chemical syntheses of spinel starting materials[1,4] were developed at the University. These materials, when custom hot pressed at moderate temperatures and high pressures *in vacuo* by Eastman Kodak Company, were shown as early as mid-1966[5] to be capable of producing substantially transparent 1 in. dia discs. During late 1966 and early 1967, still larger shapes, ~2 in. dia by 1/2 in. thick, were custom hot pressed by Kodak for N. C. State University for use in ARO-D sponsored research concerned with strengthening of spinel at high temperatures.[6]

At least a few of the larger specimens produced from starting materials made at the University and subsequently hot pressed by Kodak attained a relatively high degree of transparency. They were, however, reddish in color due to sulfur residues.[5,6] In mid-May, 1967, the sponsoring agency (ARO-D) was informed that, though much remained to be done in terms of attaining consistent optical quality, transparent polycrystalline spinel appeared to be technically feasible, and that it appeared to have considerable potential as a candidate material for transparent armor.[7]

Subsequent work demonstrated the feasibility of fabricating larger shapes by hot molding, utilizing a proprietary Kodak process (open die hot pressing or *hot molding*) in which the preformed material is subjected to less lateral restraint than in conventional hot pressing. In hot molding, there are far fewer limitations on sizes and shapes which can be successfully formed, in that there is much less dependence upon sizes of available ingots and attainable strength levels for refractory metal die components. Small lots of ~2 x 4 x 1/4 in. finished spinel tiles were successfully custom hot molded by Kodak for the University from two quite different starting materials.

In the first series, sulphate-derived spinel particulates deliberately doped with sapphire whiskers were hot molded, producing blanks from which test specimens were subsequently cut for studies of high temperature strengthening and toughening in whisker-reinforced spinel.[3,8,9] Some sulfur discoloration (a characteristic maroon red) was present, but, even so, substantial transparency was attained both in the undoped control and in those containing small concentrations of whiskers (0.1 and 1.0 volume %).

Thereafter, a modest quantity of a prototype commercial grade of spinel was made available to the University by its manufacturer, W. R. Grace & Co. This material, identified as Lot S-2 DBM, was also hot molded by Kodak, producing several 2 x 4 x 1/4 in. finished shapes, which were then furnished to Dr. John W. Taylor, Los Alamos Scientific Laboratory[10] for use in dynamic (Hugoniot) yield measurements and related impact studies. The Grace S-2 material was nonstoichiometric (MgO-rich) and had rather

different flow characteristics in the Kodak hot molding process. Within
the limited number of tries (11 in all), it did not achieve the degree
of transparency attained earlier with the N.C.S.U. sulphate-derived
material. However, sound, dense pieces verging on transparency were
produced having microstructures characterized by very fine grain sizes,
typically ~0.2 μm.

In essence, this study has been directed toward achieving trans-
parency in nominally pure (undoped) polycrystalline spinel by hot molding
and/or rate controlled sintering. Both methods tend to optimize the
densification process at the lowest possible temperatures, and conse-
quently each of them offer the prospect of achieving full densification
with minimum grain growth. However, because temperatures are kept as
low as possible (thus suppressing diffusional processes responsible for
grain growth), success by either method tends to be strongly (perhaps
critically) dependent upon the (surface area/energy) particulate
properties and high temperature flow characteristics of the starting
materials. These powder properties, in turn, are quite sensitive to
both chemical constitution and processing history.

On the other hand, fine and uniform grain sizes have consistently
been demonstrated to correlate well with increased strength and even
ballistic performance in ceramics,[11-13] generally in accordance with the
Petch relationship[14]

$$\sigma_f = \sigma_o + Ku^{-\frac{1}{2}}.$$

Thus, the methods employed in this study offer, along with the
potential hazards of their heightened materials sensitivity, the
possibility of direct and significant optimizations of the ultimate
mechanical properties of the ceramic shapes being produced. In these
respects, the basic direction followed in this investigation has
differed substantially from that of others aimed at achieving trans-
parency in polycrystalline spinel by conventional hot pressing,[15,16]
arc melting and related fusion techniques,[17] or conventional (isothermal)
sintering.[18-20] In these other studies, much higher temperatures gener-
ally have been employed, frequently in conjunction with some deliberate
doping with additives to serve as sintering aids, e.g., by facilitating
liquid phase transport. Transparency has been achieved with various
degrees of success by both hot pressing and sintering in some of these
studies. However, it is not surprising in view of the temperatures,
atmospheric environments and dopants employed, that the resulting grain
sizes have tended to be quite large, being typically two to three orders
of magnitude greater than that of the N.C.S.U.-Kodak hot molded spinel.

Unfortunately, and for a variety of reasons, the critically
important spinel starting materials (calcined spinel powders) did not
emerge from the University's synthesis efforts at the intended quality
levels. The large quantity of material produced in the final weeks of

the active experimental program was substantially inferior in terms of cation stoichiometry and sulphur content to several earlier small-batch lots.[3-5,8] Consequently, the later densification phases of the program had to contend with poor quality, gas-laden material, which created many unexpected problems in hot molding.

Important new insights were obtained into the kinetics of densification during sintering of spinel under nonisothermal conditions. The kinetic data presently available are confined primarily to the range 60 to 90% of theoretical density, over which linear densification rates could be experimentally maintained. For a variety of reasons, it was not possible under this program to carry out the final experimental optimizations by means of rate control concepts in achieving full densification of spinel by sintering. [It should be noted that such rationales for optimization of sintering have now been successfully demonstrated experimentally for polyphase ceramics and, most recently, as a means of attaining dense high alumina ceramics with exceptionally fine, uniform grain sizes].

It is the purpose of this report to outline the technology, to describe the results, and to examine some of the factors which contributed to the unexpected problems and difficulties encountered. Finally, some interpretations of the technical findings - in consonance with other ongoing research studies - are advanced.

PLAN OF WORK

In keeping with the project scope, experimental effort under this program was organized, and will be described in subsequent sections, in terms of three interrelated phases. The tasks undertaken by the various participating organizations are summarized below.

Phase I: Powder Synthesis

Under the first phase, University personnel undertook to scale up an existing (at that time, patent pending) small-batch process[4] for chemical synthesis of a suitable spinel precursor, and to provide for its semi-continuous calcinations, thus converting the precursor salt to the mixed oxide, spinel. Since the personal analytical skills and laboratory facilities which had played a significant role in Dokuzoguz's original development of both chloride[1] - and sulphate[4]-derived spinels were no longer available at the University, arrangements for analytical services were made with an experienced outside vendor, widely recognized as a source of reliable wet chemical and spectrographic analyses of ceramics and related materials.

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Phase IIA: Hot Pressing

Under Phase IIA, materials generated under Phase I were densified
by hot molding (open die hot pressing) at moderate temperatures (~1200°C)
and high pressures (~25,000 psi), using refractory metal tooling oper-
ating *in vacuo*. Since very robust equipment (far beyond the University's
hot press capabilities) is required to maintain such conditions on a
large specimen (>8 in.^{2}), this phase of the work (which to a considerable
degree made use of Kodak's existing facilities and proprietary processes)
was carried out by Eastman Kodak Company. Larger runs were preceded by
and supplemented with a number of trial runs in a smaller (1 in. dia)
hot press under comparable conditions, permitting evaluation and some
degree of optimization of the densification behavior of specific lots
of starting materials.

Phase IIB: Rate Controlled Sintering

Under Phase IIB, effort was focused upon an optional densification
method (rate controlled sintering), considered potentially capable of
achieving densification (and possibly transparency) in spinel at lower
unit costs and with fewer restrictions on sizes and shapes than is the
case with hot pressing. This novel approach to sintering stems from
earlier theoretical[5,21] and experimental[22] studies in this laboratory.
This extension of rate controlled sintering to spinel was carried out
by its original co-developer, D. R. Johnson, for whom the work accom-
plished under this program served as a doctoral dissertation topic.[23]
Though it was not possible in the critical last weeks of this project
to extend Johnson's investigation of the linear densification rate
regime (~60-90% of ρ_{th}) to a fully optimized, multiranged, rate
controlled sintering program capable of dealing effectively with final
stage densification, such programs have been found effective for other
materials. Significant advantages, especially with respect to reduction
of fired grain size and grain size distribution, have recently been
reported for rate controlled sintering of dense high purity alumina.[24]

Since it was obvious that material from Phase I would not become
available until relatively late in the program, the kinetic studies
which formed the principal part of Johnson's work were carried on with
a small quantity of a prototype commercial spinel material* having
composition and particulate properties generally comparable with
earlier "good" lots of sulphate-derived spinel.[3,6,8]

---

* Spinel powder, presumed to be nitrate-derived, identified as Lot S-2
DBM, made available *gratis* by Dr. D. G. Wirth, Washington Research Center,
W. R. Grace & Co., Clarksville, Maryland.

EXPERIMENTAL EQUIPMENT AND PROCEDURES

Phase I

Three principal functions were undertaken in Phase I: (1) synthesis of a spinel precursor from the respective sulphate salts ($MgSO_4 \cdot 7H_2O$ and $Al_2(SO_4)_3 \cdot 18H_2O$) by a cocrystallization process (2) initial drying and partial dehydration of the damp, cocrystallized precursor containing mixed sulphate salts together with the double salt, $MgAl_2(SO_4)_4 \cdot xH_2O$) and thereafter, (3) calcination of the precursor, to remove both the residual water of hydration (as H_2O vapor) and sulphur (presumably as SO_3 gas) and to convert the product into the stable mixed oxide, magnesium aluminate spinel ($MgAl_2O_4$). The principal problems involved were considered to be:

(a) Obtaining an intimate initial mixture of the sulfates with an exact stoichiometric ratio. In principle, this is done by proper batching (on the basis of adequate analytical data), then melting (to form a saturated, hot mixed salt solution), and finally, solidifying by rapid cocrystallization.

(b) Dehydrating the cocrystallized salt mixture – without remelting – to produce a friable product of reasonably high particle density. This intermediate product must be rather finely divided to allow easy escape of SO_3 during decomposition; however, individual particles should have reasonable density to reduce bulk and dusting.

(c) Decomposition of the dehydrated sulfates with complete removal of sulfur but without excessive sintering or undue loss of free surface area of the product.

(d) In all steps, maintaining high purity of material – particularly avoiding contamination with metallic ions and/or silica.

(e) In all steps, maintaining efficient materials handling to achieve reasonably high production rates. In this regard, the calcining stage was considered to be the most time consuming.

(f) Finally, avoiding air pollution from SO_3 fumes.

Cocrystallization

Figure 1 schematically illustrates the steam heated 30-gallon polyproppylene mixing vessel in which the starting magnesium and aluminum sulphate hydrate salts were batched, intimately mixed, and converted to a hot concentrated aqueous solution prior to cocrystallization. The hot concentrated salt solution was transferred (in initial runs by the drain valve illustrated, and thereafter by ladling) into heavy-duty aluminum foil trays (~20 1/2 x 12 1/2 x 1 1/2 in.) to a depth of ~3/4 in.

Figure 2 is a flow chart illustrating the cocrystallization and dehydration steps of the process, as determined on the basis of prior work,[3,4,5,8] additional preliminary studies, and early operational experience. The indicated batch size represents a practical working limit for the available facilities, and is designed to yield ~11 lb. of calcined spinel

6

MOTOR

SHAFT (TEFLON COATED)

POLYPROPYLENE LID

POLYPROPYLENE TANK

LIVE STEAM

GASKET

WOODEN COVER

METAL DRUM

VENT

GLASSWOOL INSULATION

POLYPROPYLENE TUBE

STEAM

PROPELLER (TEFLON COATED)

POLYPROPYLENE DRAIN VALVE

$MgSO_4 + Al_2(SO_4)_3$ (CRYSTALINE SOLUTION)

STAND

STEAM TRAP

CONDENSATE
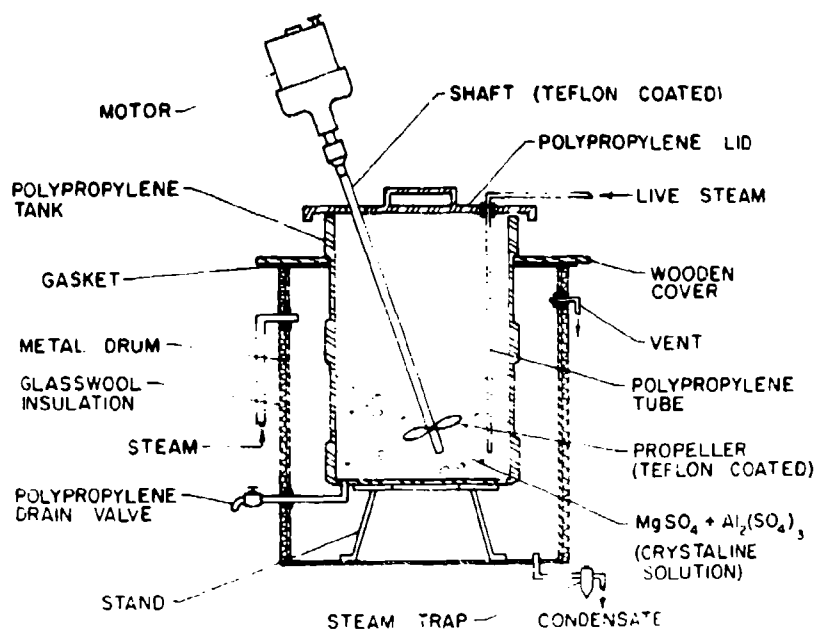
Fig. 1.   Heated 30 gal. mixing vessel for preparation of molten mixed
          sulphate hydrates (spinel precursor salts).

(including fines). The crushing and screening procedures employed were
very inefficient, resulting in as much as 40-50% of the total being
screened out as fines in the next-to-last step. With the existing
facilities, requiring largely manual operation, one such batch of pre-
cursor could be produced in two 24 hr days, but only under maximum
effort, consuming at least 2 man-days of labor per day.

Drying

     Existing cabinet dryers (steam heat for 1st stage, electric for 2nd)
were utilized, with the product being handled in the aluminum trays.
The soft "cake" which developed during the first drying stage was manually
broken into coarse lumps, providing better air circulation, thus
facilitating heat and vapor transport. Remelting during drying, with
attendant densification (vitrification) which slowed drying and hampered
later crushing of the product, was a not uncommon occurrence in these
manually controlled dryers. Installation of temperature controller-
programmers could have eliminated remelting prob.ems, as well as increasing
drying efficiency.

Crushing and Screening

     Well dried (second stage) material is hard and tough, and the dust
generated during crushing and screening is irritating to skin, eyes, and
nostrils. These rather time consuming operations were performed manually
by personnel who wore protective gloves, goggles and/or breathing masks.
Though it would have been very desirable in the interests of efficiency
and quality control, it was not feasible within the limits of this program
to install an appropriate closed, mechanised materials handling system.

*Analyze Starting Materials
↓
Heat Vessel
(steam jacket)

*Add ~18.4 lb. ————————→ ←———————— Add live steam
MgSO₄·xH₂O   1st Melt

*Add ~46.3 lb. ————————→
Al₂(SO₄)₃·yH₂O   Agitate, Continue Heating
(Slowly)

↓ ←——————— Add boiling distilled H₂O
**Complete Melt
(saturated aqueous solution, ~95°C)
↓
Pour into Pans
↓
Cocrystallization
(spontaneous upon cooling)
↓
1st Dryer
↓
~1 day at 40-47°C
————————→ Remove water vapor
Break to Lumps
↓
~1 day gradually increasing to ~110°C
————————→ Remove water vapor
2nd Dryer
↓
~1 day, 110° to ~300°C
————————→ Remove water vapor
Dehydrated Cocrystals
↓
Double Roll Crusher
(teflon coated)
↓
Plastic Screens
————————→ Remove Fines
Coarse Fraction
(-6, +20 mesh)

Fig.   Fig. 2.   Flow chart for synthesis of spinel precursor.

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* Actual quantities depend upon raw material analyses for cation
   stoichiometry and water of hydration.
** Proper point for on-line verification and/or correction of cation
   stoichiometry (if timely analyses are available).

8
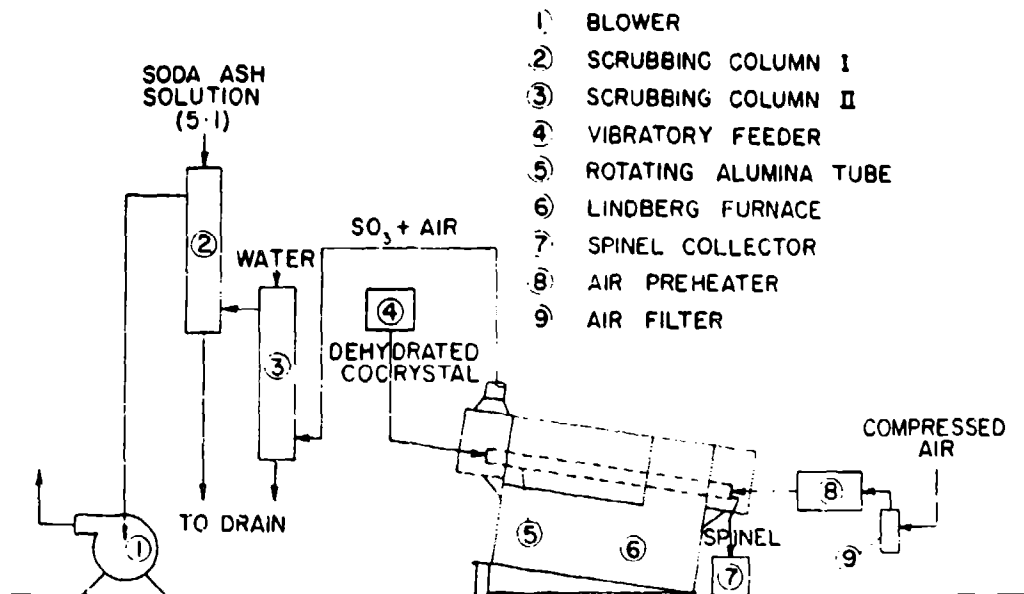
Fig. 3. Schematic diagram for dynamic calcining furnace and effluent gas scrubber.

Dynamic Calcination

A six-foot long Lindberg four zone diffusion furnace was extensively modified to provide an inclined, rotating tube counterflow calcining system. This unit, including a cascaded scrubber system to remove SO₃ gases from the stack effluent, is schematically illustrated in Fig. 3. The two-inch I.D. by seven-foot long mullite tube was supported in double collet clamps and bearings designed to accomodate thermal expansion, out-of-roundness, and camber without undue stress on the tube (see Fig. 4). Both the angle of inclination and rotation rate could be varied over wide experimental limits. Inlet and exhaust plenum chambers enclosed both ends of the tube, and provided for controlled introduction of prefiltered, preheated air to sweep products of decomposition through the tube, and for collection and removal at the exhaust end (see Fig. 5). A vibratory feeder (Fig. 5a) introduced predried and sized cocrystallized sulfate feed material at the high end and a collection system permitted gravity removal of the calcined material at the lower end (Fig. 5b). A complete set of working drawings for all components fabricated by N.C.S.U. in modifying this furnace were furnished to the sponsoring agency.

(a)   (b)
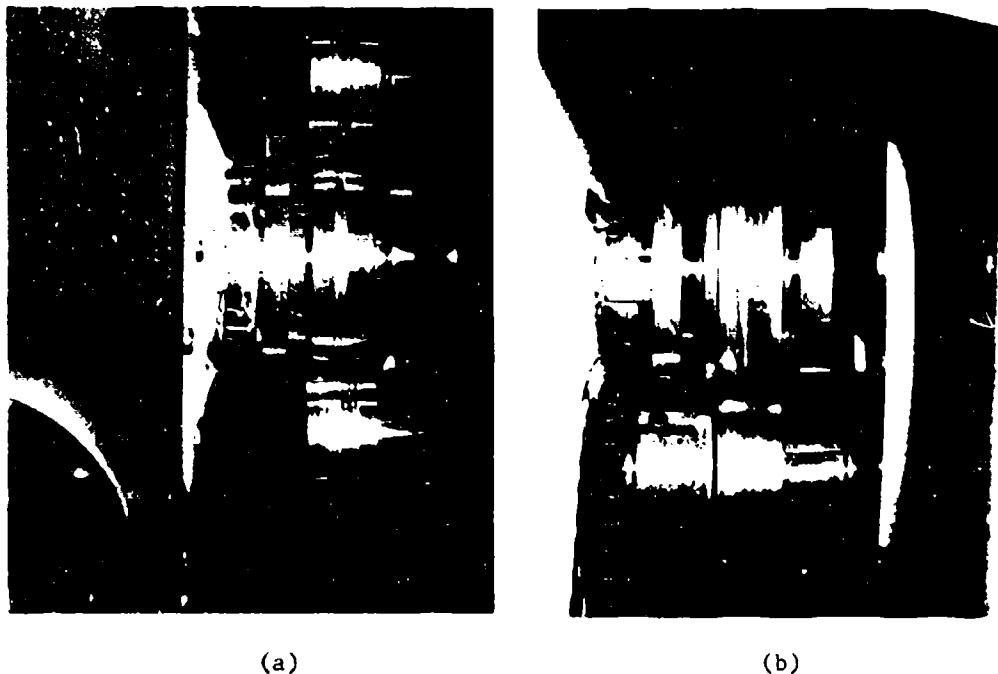
Fig. 4. Inclined rotating tube drive details (a) upper thrust/idler
bearing-drive unit (left view); (b) lower idler bearing-
expansion/camber runout unit (right view). Mullite tube is
seven feet long (axis shown horizontal in these views),
supported by and centered in the double collet grips. Thick
Fiberfrax paper cushions and insulates tube beneath collet, and
also is used for iris gaskets through which tube enters plenum
chambers.

Phase IIA

All hot pressing and hot molding runs were carried out by Eastman
Kodak Company, making use of their own existing facilities and processes.
Though they have for obvious reasons wished to protect some proprietary
company interests, Kodak personnel have in the past been very cooperative
in providing adequate information to permit realistic reporting of
processing history[3,6,8] and in this study, to facilitate planning of future
runs and rational reporting and interpretation of results.[26-29]

In view of the marked densification rate sensitivity observed for
spinel in comparable temperature ranges in rate controlled sintering
studies under Phase IIB[23], it is appropriate to note that Kodak's hot
pressing/hot molding facilities do not appear to be instrumented for
strain (punch travel) - strain rate data and/or control. For this reason,
it has not been possible in this (or in earlier cooperative studies[6,8,10])
to properly evaluate the concept of rate controlled densification[2,3,5]
during hot molding of this material, even though spinel is known to be a
prime candidate for this kind of control because it is both gas-retentive
and strongly rate sensitive in its plastic yielding behavior.
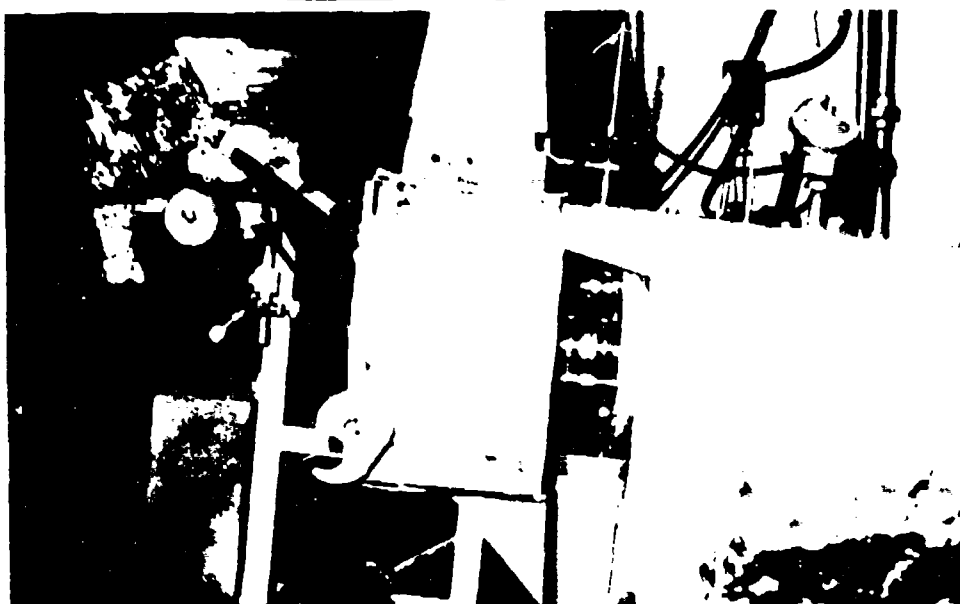
(a)
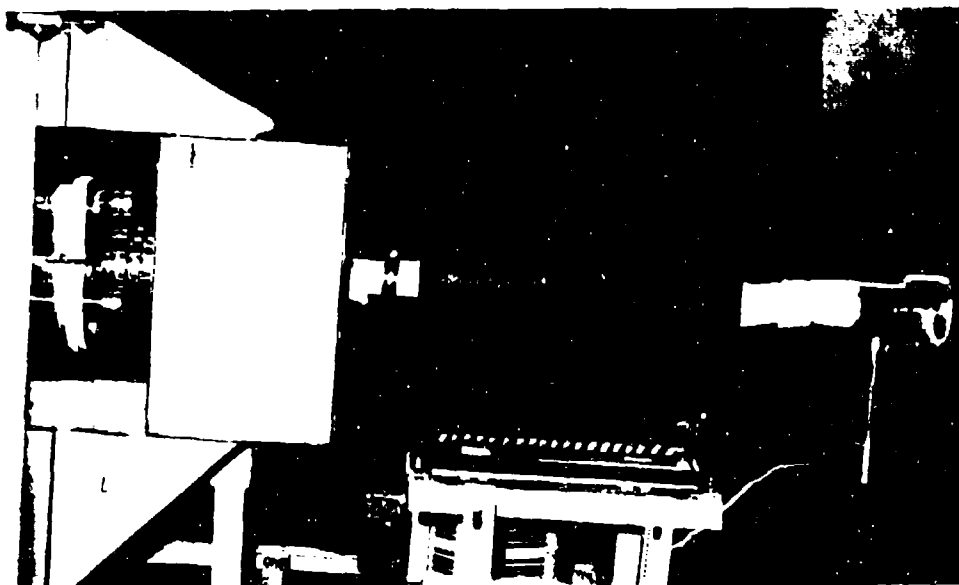
(b)

Fig. 5. Inlet and exit plenum details (a) upper plenum, stack outlet,
and vibratory precursor feeder (teflon coated bowl); (b) lower
plenum, product discharge (vertical alumina tube), and air
preheater. Sightglass (extreme right) permitted visual
monitoring of material moving along tube axis.

Phase IIB

Rate Controlled Sintering Furnace and Control Equipment

As described by Johnson, "Process control in experimental rate controlled sintering differs from that in conventional sintering by the reversal of the roles of the normally independent (temperature) and dependent (densification rate) variables. In rate controlled sintering, densification rate is independently controlled and the resultant temperatures and time rate of change of temperature are measured. This unique method of process control requires special equipment and instrumentation".[20]

The apparatus used (see Figs. 6 and 7) has been under development at N.C.S.U. for several years, and has been described elsewhere, from initial concept,[21] through development and refinement,[28,29] and active experimentation.[22-24] For the purposes of this program, some new components were added and minor alterations were made, principally to simplify and improve instrumental manipulations, and to provide an alternate high temperature (~1700°C) furnace for achieving very rapid densification rates, and an alternate, slow speed motor for the DataTrak programmer for controlling very slow densification rates.
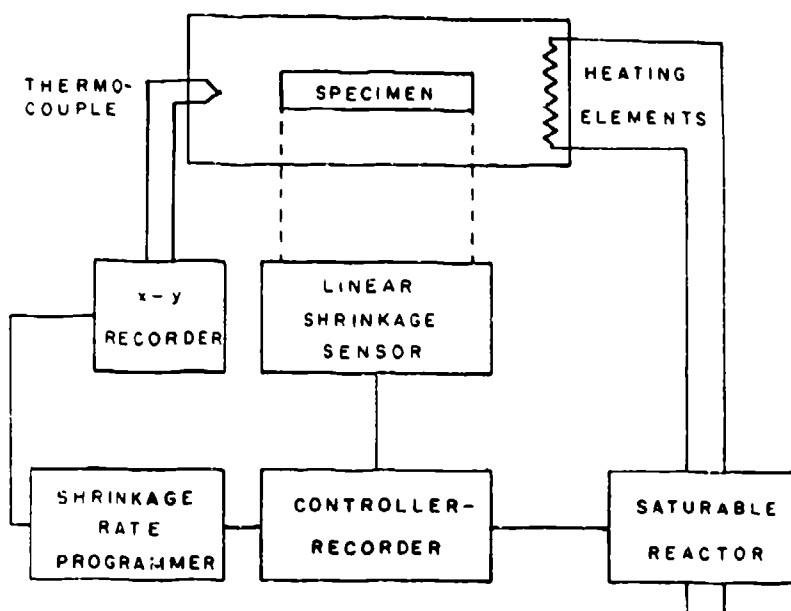
Fig. 6. Schematic diagram of programming/controlling and measuring instrumentation for rate controlled sintering (After Ref. 21).
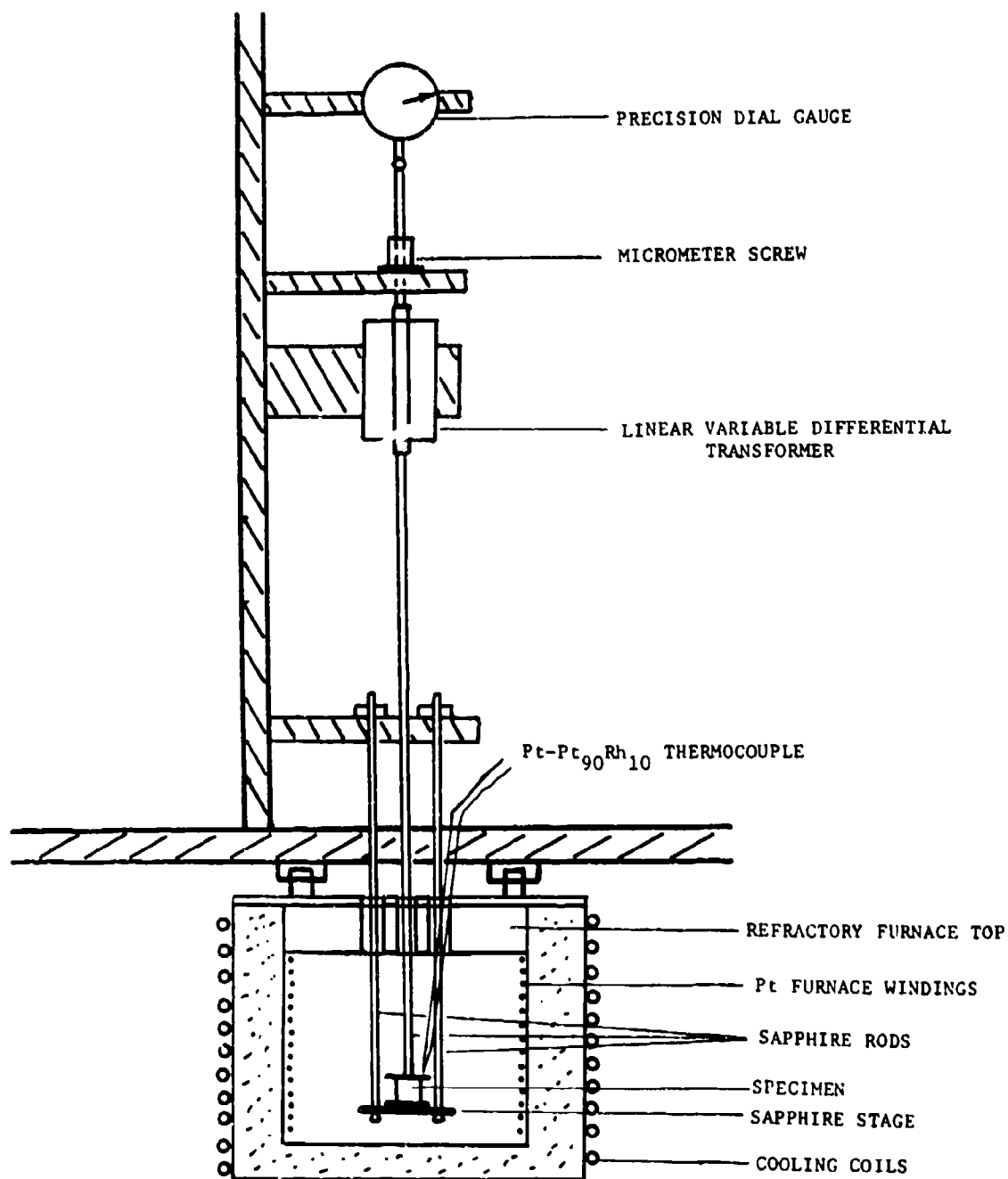
Fig. 7. Sectioned schematic of rate controlled sintering furnace showing sample holder and shrinkage sensor (After Ref. 23).

Table 1. Starting Materials

Manufacturer's Designation	Baker and Adamson Magnesium Sulfate Crystals ACS Code 1924	Baker and Adamson Aluminum Sulfate Crystals, ACS Code 3241
Chemical Formula	$MgSO_4 \cdot 7H_2O$	$Al_2(SO_4)_3 \cdot 18H_2O$
Dehydration and Decomposition (Handbook Data)	m.p. $(-6H_2O)$ 150°C b.p. $(-7H_2O)$ 200°C $MgSO_4$ d. 1124°C	m.p. $(-18H_2O)$ 86.5°C $Al_2(SO_4)_3$ d. 770°C

Cation Impurities[*]
(spectographic analyses, ppm)

Al	–	(Major, >10%)
Ba	–	6
Cu	15	12
Mg	(Major, >10%)	7
Si	6	7

Quantitative Analyses, %[†]	(Range of 5 samples)	(Range of 7 samples)
Al	–	8.52 – 8.81
Mg	10.06 – 10.70	–
SO_4	39.62 – 42.40	47.64 – 48.60
$Al_2(SO_4)_3$, anhydrous	–	56.22 – 59.33
$MgSO_4$, anhydrous	49.68 – 52.90	–
Loss on Ignition at 1300°C, %[††]	83.48	83.34

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[*] External Analytical Service Laboratory, B 303 (cont.), 9/8/69; [†] B 303, 8/20/69; [††] C 782, 1/7/70.

MATERIALS

Since spinel constitutes only about one sixth of the weight of original starting material, for Phase I it was necessary to obtain substantial quantities, 200 lb. and 500 lb. respectively, of the required reagent grade magnesium and aluminum sulfate hydrates. The basic chemical data pertinent to these specimens is given in Table 1. Upon receipt, these very hygroscopic materials were carefully transferred to tightly sealed plastic bags in convenient quantities for storage, hopefully minimizing atmosphere-related variations in water content. The magnitude of such variations, and their potential deleterious influence upon precision batching to obtain an exact $MgO:Al_2O_3$ stoichiometry, is indicated by the range of values reported for five and seven samples, respectively, of these bagged materials.

Prereacted spinel materials produced by another process, presumably from nitrates, were made available *gratis* by the manufacturer, W. R. Grace & Co., for use in portions of the work undertaken in Phases IIA and IIB. Table 2 summarizes the available analytical data for these materials.

Table 2. Prereacted Spinel Materials Obtained from W. R. Grace & Co., Clarksville, Maryland

	Lot S-2*	Lot S-2 DBM*	Lot S-5570†
MgO:Al$_2$O$_3$ mol ratio	1.086	1.062	1.003
Impurities, ppm			
Fe$_2$O$_3$	140	110	Fe 66 - 79
MnO	2	2	-
SiO$_2$	40	320	Si 6 - 10
CoO	nd (<10)	nd (<10)	-
Na$_2$O	30	30	nd (<500)
TiO$_2$	50	80	-
ZrO$_2$	nd (<40)	nd (<40)	-
B$_2$O$_3$	3	3	-
NiO	40	40	-
N	<50	<50	-
			Cu 6 - 10

* External Analytical Service Laboratory, A 248, 6/10/69; † Analysis courtesy W. R. Grace & Co.

RESULTS AND DISCUSSION

Phase I: Synthesis of Precursor

Stoichiometry

From Fig. 2, it is obvious that, apart from accidental contamination, the cation components of the chemical constitution of the spinel and, thereafter, of the densified spinel ceramic essentially become fixed at the time the hot molten salt is cocrystallized. In later stages, cation stoichiometry cannot be changed significantly, except possibly by blending of batches which differ in MgO:Al$_2$O$_3$ ratio. It is also apparent that very precise and reliable analyses of the starting materials are required if the desired stoichiometry is to be attained reproducibly. However, as indicated by Table I and its associated text, a considerable spread in the available data was encountered; presumably, such variations can be attributed to (1) the materials, (2) the sampling procedures and/or (3) the accuracy and reproducibility of the analyses. As often is the case, even after much work has been done, it is not really possible in this instance to be certain which of the three factors dominate. However, it is clear that, for whatever reasons, uncertainties associated with the

Table 3. Comparisons of Analyses for Two Trial Lots of Cocrystallized Spinel Precursor

| | Sample A | | Sample B | |
	Analysis 1*	Analysis 2†	Analysis 1*	Analysis 2†
SO_3	53%	61.2%	54.0%	55.69%
MgO	8.9%	5.36%	7.7%	7.58%
AlO	17.8%	19.5%	18.5%	18.05%
MgO/Al_2O_3 ratio	1.28	0.696	1.065	1.069
% solids (ignited @ 1100°C)		25.01%		25.87%
Agreement between Analyses	Poor		Good	

* External Analytical Service Laboratory, B 882, 10/10/69; corrected 11/10/69; † Check analyses courtesy Dr. N. Levy, Jr., W. R. Grace & Co., 11/10/69.

actual quantitative oxide content (MgO and Al_2O_3, respectively) of the starting sulphate salts - and of the resultant stoichiometries (see Table III) - persisted throughout this study. These uncertainties, coupled with other operational factors, ultimately led to overcompensation for apparent prior errors in batch formulations, and contributed to unexpectedly poor control of cation stoichiometry. The first large lot of precursor salt, identified as Batch 8, was formulated for 1:1 stoichiometry on the basis of all analytical data then avilable. However, as shown by Table 4, it was found to be quite alumina-rich; again, batch yields were in apparent disagreement with batch formulations. At this juncture, fresh specimens of the starting salts (which had been stored in plastic bags in the open laboratory environment for about five months) were sent for new analyses, to include loss on ignition at 1300°C (see Table 1). [In addition, a new lot (Batch 9) was made, with the formulation having been shifted toward magnesia, apparently compensating for the alumina-rich report from Batch 8.]

Table 4. Cation Stoichiometry of Four Production Batches of Spinel Precursor

| | Batch 8* | Batch 9† | Batch 11† | Batch 12† |
	(calcined)	(precalcined)	(precalcined)	(precalcined)
MgO	24.87%	9.39%	9.55%	8.86%
Al_2O_3	75.88%	20.74%	20.74%	20.38%
$MgO:Al_2O_3$ mol ratio	0.829	1.155	1.164	1.100

* External Analytical Service Laboratory, C 782, 1/7/70; † D 154, 2/13/70.

Table 5. Formulation and Resulting Stoichiometry of Large Production
Lots of Spinel Precursor.

Date	Identity	Batch Weights, lb.		Initial Weight Ratio	Final Mol Ratio
		Magnesium Sulphate	Aluminum Sulphate		
12/8/69	Batch 8	17.59	46.506	0.3782	0.829
12/30/69	Batch 9	18.738	46.416	0.4037	1.155
1/7/70	Batch 10*	19.19	46.506	0.4126	--
1/16/70	Batch 11	18.84	46.133	0.4084	1.164
1/21/70	Batch 12	18.84	46.645	0.4039	1.100

* During ladling of the hot melt, the operator noted undissolved
"nodules" of material in the bottom of the vessel; he quite properly
recommended it not be analyzed, calcined, or used. From its initial
weight ratio, it seems likely that Batch 10 was supersaturated with
magnesium sulphate; graphical estimates (see text) indicate that the
final mol ratio would have exceeded 1.20.

In evaluating the additional analytical information, the operator
responsible for the cocrystallization process concluded that stored
aluminum sulphate had remained essentially unchanged, whereas magnesium
sulphate had changed (presumably by equilibrating with atmospheric
moisture) during the storage period. It is now apparent from the records
that, lacking additional analyses and being under considerable time
pressure, the operator arrived at a 2.46% additive correction factor
which was applied to the magnesium sulphate content of all remaining runs
(Batches 10-12).

Table 5 summarizes the initial formulations and the resulting
stoichiometric ratios (from *post facto* analyses) for Batches 8-11.
Recent reevaluations of these data have shown that, when treated
graphically (not illustrated), they correspond rather well with a simple
linear relationship of the form

$$y = a + bx$$

where x   initial weight ratio
      y - final mol ratio
      a = intercept constant (~5.905)
      b = slope constant (~17.77).

Based upon this admittedly empirical analysis,* to achieve the desired
1.00 mol ratio the initial weight ratio should have been ~0.391 (±~0.0025).

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* The observed linear relationship appears to support the relative
   reliability of the   earlier stoichiometric analyses (see Table 3);
   the trends (slopes) appear to be correct, but offsets may well exist
   for quantitative values.

This value is in reasonable accord with a revised weight ratio of 0.3988 recommended on Jan. 16, 1970 by the cognizant staff scientist on the basis of his review of the Jan. 7, 1970 analytical data (Table 1). His calculations indicated that the starting materials were actually $MgSO_4 \cdot 6.87H_2O$ (not $\cdot 7H_2O$) and $Al_2(SO_4)_3 \cdot 15.3H_2O$ (not $\cdot 18 H_2O$). Unfortunately, these more precise calculations and the recommended weight ratio of starting materials did not reach the operator concerned in time to influence the formulation of any of the large production batches.

Purity

As mentioned in the preceding section, the condition at cocrystallization not only determines stoichiometry, it also has a major role in determining purity. In general, subsequent handling can only add cation contaminants, not remove them (this point is discussed again in a later section). Therefore, it was of some concern to determine impurities present in starting materials, and if possible to eliminate them prior to cocrystallization.

The spectrographic data given in Table 1 relate to the respective sulphate hydrate salts, (i.e., a very dilute form of the final product) and constitute a rather insensitive measure of the impurities which will be found in the much more concentrated oxide forms. For this reason, additional analyses of cation impurities were obtained on starting materials which had been ignited at 1300°C; the results are given in Table 6. It is evident that the magnesium sulphate is much cleaner than the aluminum sulphate, and that the latter, making up the bulk of the batch, dominates the impurity content of the calcined product. Sodium (Na) appears to be the only significant process-related contaminant. The operator noted that the aluminum sulphate contained readily visible insoluble "trash"; this had been previously observed in earlier studies,[68]

Table 6. Cation Impurities in Starting Materials and Calcined Spinel.

Element*	$MgSO_4$ ACS 1924 ignited @ 1300°C	$Al_2(SO_4)_3$ ACS 3241 ignited @ 1300°C	(Batch 8, IRTCF 13)
Ag	1	3	1
Al	5	Major	Major
B	25	10	1
Ca	10	5	–
Cr	–	5	5
Cu	10	25	10
Fe	–	250	250
Mg	Major	100	Major
Mn	–	10	10
Na	–	50	500
Si	5	50	25

* Concentration in ppm unless otherwise noted; C 782, 1/7/70.

working with salts of comparable quality obtained from another vendor.
Whereas in earlier work it had been possible to remove the "trash" by
filtration,* there was very little hope of doing so from the direct-
melted batches produced in this program.

Phase I: Dynamic Calcination of Dehydrated Precursor

<u>Optimizing and Operating the Dynamic Calcining Furnace.</u>

The inclined rotating tube calcining furnace (IRTCF), described
earlier, is a relatively complex device with a number of *independent*
controls, e.g., for temperature, rotation rate, stack draft, air counter-
flow, etc. Under dynamic conditions, they give rise to a whole set of
interdependent operating parameters which combine to influence markedly
the local conditions to which the material is subjected at various
points along the tube length, the stability of its patterns of movement
through the furnace, as well as what is done to it in terms of thermo-
chemical treatments. These parameters were studied in a series of pre-
liminary runs of a few minutes to at most a few hours duration. It
was found rather quickly that a favorable set of conditions existed
(described later) wherein the whole dynamic system could be operated
under essentially stable conditions. When dynamic stability was attained,
the principal preturbations of concern (which could be detected and
cleared by the operator) were occasional sticking or jamming of feed
materials in the feed tube or near the upper (entrance) end to the
rotating tube itself. To attain this much-needed stable mode of operation,
two conditions relating to the feed material had to be satisfied:
(1) the material had to be sized relatively coarsely, ~-6 mesh, and
substantially free of fines (~-20 mesh), and (2) the material had to be
precalcined to ~650°C. This latter condition, which removed most of the
water of hydration, was necessary to avoid forming an almost unmanageable,
highly corrosive effluent, equivalent to fuming sulphuric acid, which
had devastating effects upon the upper plenum chamber and stack components.

Since no other suitable facility for precalcination was available,
the dynamic tube furnace (IRTCF) was employed; thus each lot of material
made two separate trips through the tube, (1) to precalcine, removing
H_2O @ ~650°C, and thereafter (2) to remove nominally anhydrous SO_3
@ ~1145°C. Typical operating conditions for each case are given in
Table 7.

Weight loss (principally H_2O) in precalcining is about 33%; for
final calcination the loss (principally SO_3) is ~80%. These very sub-
stantial weight losses are accompanied by (1) a solid-to-vapor change
of state, (2) expansion of the vapor as it comes into equilibrium with

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* The Palmour-Dukuzoguz patent[4] teaches (1) preparation of a cold,
dilute aqueous solution of the starting salt, (2) filtration to remove
tramp impurities, (3) concentration by evaporation (simmering), and
finally, (4) cocrystallization by chilling.

Table 7.   Typical Operating Conditions for Inclined, Rotating Tube
Calcining Furnace.

Slope	RPM	Temperatures, °C					Avg. Feed Rate g/hr	Avg. Product Rate g/hr
		Zone 1	Zone 2	Zone 3	Zone 4	Air Preheater		
				Precalcining				
1:12	6	360	370	500	660	~950	625	416
				Calcining				
1:12	3	740	880	1130	1145-1150	~950	585	147

the heated tube.   Under dynamic conditions, both factors contribute to
very large volumes of expanded vapor, which move up the tube at
relatively high (at times almost explosive) velocities, sufficient to
entrain and blow back fines at the upper (feed) end.   By contrast, the
lower portion of the tube, in the hottest zone, is relatively quiescent,
marked by gentle thermal convection currents.   Best handling of the
counterflowing gases was obtained by keeping the entire system (plenums,
tube, and product collection bag) under moderate negative pressure
through proper regulation of the forced draft scrubber fan damper and
the excess air inlet at the upper plenum stack.   Under these conditions,
sufficient air (filtered through a glass wool plug) was aspirated
through the air preheater, so that pressurized air was not required.

With properly sized feed material, excellent tumbling action was
obtained; the rolling, tumbling material covered an almost ideal ~120°
segment of the tube circumference.   This vigorous action provided for
very rapid thermal equilibration and repeated exposures of each granule
to the "free surface" of the bed, directly in contact with the counter-
current gas stream.   Transit times through the furnace varied somewhat
with granule size, faster for large grains, slower for small.   On the
average, under calcination conditions, transit times were in the
25-30 minute range, resulting in hot zone (peak temperature) residence
times estimated at 5-8 minutes.   Optical pyrometer readings taken directly
on granules within the hot zone were consistently within a few degrees
(i.e., within the limit of observer error) of those measured by thermo-
couple on the appropriate indicator-controller.

In general, the IRTCF unit worked very well, with only minor
mechanical adjustments being required; most of them related to the small
vibratory feeder and its associated feed tube components.   The very
corrosive nature of the sulphur-laden exhaust gases created some problems
in the upper plenum chamber and eventually, in the scrubber system.   The
4 in. dia cross-section of the pyrex pipe components of the scrubber
resulted in high gas velocities at the strong negative drafts required
for stable furnace operation.   Scrubbing efficiency probably would have
been improved by   larger column cross-sections, denser packings, and
slower local velocities.

The unit was operated continuously, 24 hours per day, for a period of more than seven days (January 26-February 1, 1970) in precalcining and calcining ~30 lb. of spinel from Batches 8, 9, 11 and 12. The furnace was manned by two-man crews (who also performed some crushing and screening tasks) for 16-18 hrs per day and by an experienced person operating alone for the remaining hours.
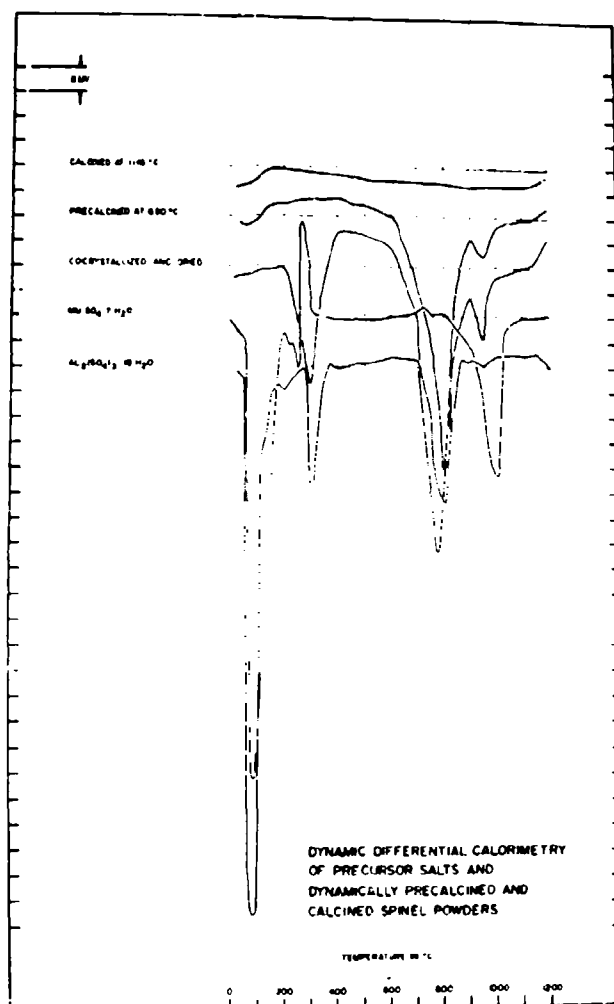

Fig. 8. Thermoanalytical characterizations of starting materials, inter-
mediates, and final spinel calcined at 1145°C. Material from
Batch 11. Dynamic differential calorimetry to 1200°C
@ 10°C/min, sapphire (Al_2O_3) reference; curves corrected for
baseline drift.

The Calcining Process

For the material in question, calcination continues and completes the process begun in Fig. 2. It relates to high temperature chemistry: (1) dehydration of the remaining water of crystallization in the starting salts, (2) decomposition of the resultant anhydrous sulphates, and (3) solid-state reaction of the remaining oxides to form the mixed oxide spinel. The sequence of events occurring during thermal treatment is indicated by the superposed thermoanalytical (DDC) traces shown in Fig. 8. The initial salts show strong endotherms at ~100°C, and later at ~250°-300°C, all associated with dehydration. The decomposition of sulphur is denoted in aluminum sulphate by an endotherm at ~800°C, and in magnesium sulphate by a more complex endotherm from about 750-1000°C, being substantially complete by 1100°C. The cocrystallized and partially dehydrated material shows a dehydration endotherm at ~300°C, a strong sulphate decomposition endotherm at ~800°C, and a less prominent one at ~950°C. After precalcination at 650°C, only the sulphate decomposition exotherms remain. Material dynamically calcined at 1145°C appears to be substantially free of any thermal activity which might be indicative of further reaction; on the basis of these data alone one would conclude that calcination was complete. A similar conclusion would be reached on the basis of x-ray diffractometer studies (not illustrated), which — for this material calcined at 1145°C — indicated well crystallized but very fine grained spinel containing some free MgO.

However, other criteria, including both chemical analyses and discolorations occurring in hot molding evaluations, clearly show that sulphur was incompletely removed. This topic is discussed in some detail in the following section.

Anion (SO_3) Removal

As indicated in the preceding section, both x-ray crystallographic and DDC analyses indicated that calcination was essentially complete at 1145°C in the dynamic calcining furnace. Table 8 shows that the elemental sulphur content of Batch 8, IRTCF 13 (initially thought to be <0.01% at the time the process was considered to be optimized and the seven day calcining run was started) was actually in the range 0.25-0.35%S by weight, equivalent to almost 1 wt. % SO_3. Had the true sulphur content been known at that decisive moment, further experiments capable of really optimizing the process at higher calcining temperatures would have been easy and timely to make, well within the thermal capabilities of the calcining furnace (max. temperature ~1400°C).

Table 8 includes data from several earlier dynamic runs, and for comparison, Zimmer's[8] static-calcined spinel having a sulphur content of 0.08%. There is no clearly discernable temperature dependence in this limited spread of data; however, there are some indications that the ease of sulphur removal may possibly depend upon the cation stoichiometry ratio, with magnesia-rich spinels being more sulphur-retentive.

Table 8. Variations in Sulfur Content of Different Spinels Attributable to Calcining Conditions and/or Cation Stoichiometry

Material	MgO:Al₂O₃ mol ratio	Calcining Procedure	Temperature °C	Sulfur Content (%S)	Source of Analysis
Zimmer spinel	~1.00	Static, deep bed	1080 (24 hr)	0.08 (0.048 after hot molding)	Table 1 of Ref. 8
Johnson spinel #2	~1.00	Precalcined, static	700	6.03	*C 458, 11/24/69
(precalcined, ~20 mesh)	~1.00	Dynamic (IRTCF #2)	1075	0.423	C 458, 11/24/69
Batch 2 (-6 mesh)	1.056	Dynamic (IRTCF #6-II)	1075	0.46	*C 501, 12/11/69
Batch 1 (-6 mesh)	1.086	Dynamic (IRTCF #7-II)	1085	0.71	C 501, 12/11/69
Batch 8 (-6 mesh)	0.829††	Dynamic (IRTCF #13)	1140	0.361†	*C 782, 1/7/70
Batch 8 (-6 mesh)	0.829††	Dynamic (IRTCF #13)	1140	<0.01 †	*C 782 (corrected) 1/7/70
Lot 08015020/11016018 (Blend of Batches 8 and 11)	.092††	Dynamic (IRTCF #18, #20)	1145-1150	0.245	*D 771, 5/20/70
Lot 08015020/11016018 (Blend of Batches 8 and 11)	1.1729††	Dynamic (IRTCF #18, #20)	1145-1150	0.235	AMMRC, cited in Table 1 of Ref. 24

* Analysis by External Analytical Service Laboratory

† In a routine check of analysis reports at the external analytical service laboratory, a very low sulfur content was erroneously reported to N.C.S.U. by telephone. Written reports indicating the likelihood of much higher sulphur content in this pivotal sample were not received by the University personnel involved until much later.

†† Lot #08015020/11016018 was carefully blended to achieve 1:1 cation stoichiometry from Batch 8 (alumina-rich) and Batch 11 (magnesia-rich) on the basis of analyses given in Table 4. Analyses of the actual blend show it to be quite magnesia-rich. Evidently Batch 8 was appreciably less alumina-rich- or Batch 11 more magnesia-rich - then the analyses indicated.

Cation Contaminants

The final products, as well as all earlier intermediates, were handled with great care to avoid as much as possible the pickup of accidental contaminants; disposable plastic gloves (protecting product and producer) were used in manual operations, and plastic bags were employed to collect, transfer, and store the product in all stages. Product purity was considered to be vulnerable to (1) airborne laboratory dirt and dust which could have been incorporated during drying, crushing, screening and other "open" operations, (2) pickup of silica from Fiberfrax debris or from the hot mullite furnace tube, and (3) other accidental sources. Since neither iron nor silicon contents increased as a consequence of handling and firing (Table 6), possibilities (1) and (2) apparently did not occur to any significant degree. However, soda content (as Na) did increase significantly. No conclusive evidence for attribution of a sodium source is available, but the best candidates are thought to be (1) airborne transport of sodium carbonate dust (even though a dense, nondusting grade was being used) from the supply tank for the second scrubber column to the precursor feeder on the furnace during periodic recharging and mixing of the sodium carbonate solution; (2) soluble salt "drip" from within the steam dryer during humid conditions; or (3) a cleaning agent residue in process equipment.

Phase I: Blending and Milling

The granular calcined product (derived from batches of differing stoichiometry) was blended to achieve uniform stoichiometry and milled to break up agglomerates. Briefly, the procedure consisted of (1) dividing a given quantity of granular product - in a sample splitter to avoid size segregation - to the approximate quantity needed for blending, (2) accurately weighing and batching in 300g quantities to achieve the best attainable stoichiometry from the requisite number of lots, (3) tumbling 2 hr in a twin shell blender - with added 96% Al_2O_3 balls and ~0.27ml triethanolamine as a milling aid - to break down the friable granules, (4) combining two 300 g tumbled lots, then fine milling for 2 hr in a 96% Al_2O_3 jar mill (1 gal. capacity) with a 4:1 ball:charge ratio, (5) tumbling again for 15 minutes to break up and disperse any "caked" material from the ball mill, and (6) screening through -20 mesh nylon to remove any remaining coarse agglomerates. This sequence, yielding ~600g of milled material, was repeated as needed to make up the required total.

Two different blends were prepared, each designed - on the basis of the available analyses - to achieve 1:1 $MgO:Al_2O_3$ stoichiometry. The first, identified as Lot 08015020/11016018-DBM-T-1 through 4, a blend of Batches 8 and 11, was forwarded to Eastman Kodak Co. for use in Phase IIA. The second, identified as Lot 811129B-T-DBM-1 through 17, totalling 20 lb., was drawn from Batches 8, 9, 11 and 12, and was forwarded to AMMRC[10,11] in compliance with a contractual requirement under Phase I.

Phase I: Characterization of Product.

For reasons discussed in the foregoing section, the quality of the product (spinel powder) fell far short of expectations. The results are compared with an earlier small-batch sulphate-derived spinel[8] in Table 9.

Table 9. Characterization of Sulphate-Derived Spinels

	*Zimmer spinel		+Lot 08015020/11016018-DBM-T	
	Powder	Hot Molded		Powder
	Values in per cent unless otherwise noted			
Al	>10	>10	(Al_2O_3)	69.48
B	0.01	0.004	(B_2O_3)	0.015
Ca	–	–	(CaO)	0.01
Cu		<10ppm	(CuO)	0.0025
Fe	0.02	0.01	(Fe_2O_3)	0.011
Ga	nd	0.006		
K	<3ppm		(K_2O)	0.003
Mg	>10	>10	(MgO)	29.96
Mn	nd	nd	(MnO)	0.01
Na	0.04	<10ppm	(Na_2O)	0.10
Ni	30ppm	–		–
S	0.08	0.048		0.245
Si	0.01	0.004	(SiO_2)	0.02
Sn	60ppm	–		–
Ti	–	–	(TiO_2)	<0.005
Zn	–	0.08		–
Zr	–	0.05		–
mol ratio	(est)~1.00			1.091
Specific Surface (BET)	25 m^2/g †			~55 m^2/g †

*Table 1 of Ref. 8

+External Analytical Service Laboratory, D 771, 5/20/70.
†Surface area measurements (Aminco Sor-BET), N.C.S.U.

Phase 2A: Hot Molding of Spinel

Preliminary Hot Pressings

Figure 9 illustrates relative opacity and/or translucency in discs
hot pressed by Kodak in preliminary evaluations of the sulphate-derived
spinel (identified as T-1 through T-4) from Phase I and of the alternate
material, Grace S-5570. As might be expected, the high sulphur content
(at least 0.6 wt % SO_3) of the Phase I material greatly hinders
densification by normal hot pressing procedures; it also produces
strong coloration, particularly when hot pressed in the presence of
carbon. When rehot-pressed (press-forged) the degree of translucency
is much improved, though far short of the rather good transparency
attained in some comparable earlier hot pressings of small-batch produced
sulphate-derived spinels (S ~0.05%).[3,5,6,8]

Hot Molding

Table 10 summarizes Kodak's efforts at hot molding 2 x 4 x 1/4 in.
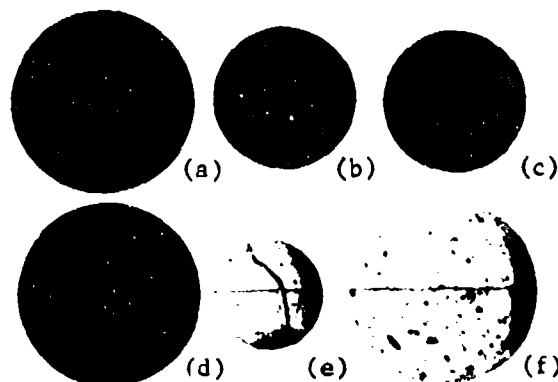shapes from these materials. Regretably, four of the best pieces

Fig. 9. Relative opacity and/or translucency of selected hot pressed
spinel discs:[25,27,29] (a) #52-53 (T-1)"Carnall method", 1200°C
@ 10 tons; opaque; (b) #60 (T-1) cold pressed @ 10 tons, heated
to 2200°F @ 10 tons, maintain 10 tons @ 2200°F for 30 min, very
dark, opaque, microhardness $K_{500} \approx 1385 \pm 65$, polished; (c)#63
(T-1) same procedure as (b), maintain 10 tons @ 2200°F for
30 min, semi-opaque, less dark, polished; (d)#118FR66 (T-2),
procedure same as (b) and (c), but rounded to 0.975 in. and
rehot-pressed (press - forged) at 10 tons @ 2300°F for 30 min,
contains healed cracks, translucent, red, polished; (e) same
as (d), but without carbon spacers, broken in two pieces,
highly translucent, much less red, polished; (f)#177 (Grace
Lot S-5570; as received, cold pressed and reground) 10 tons
@ 2300°F for 30 min, polished, 0.063 in. thick, translucent.
Specimens in contact with ruled horizontal lines, back lighted.

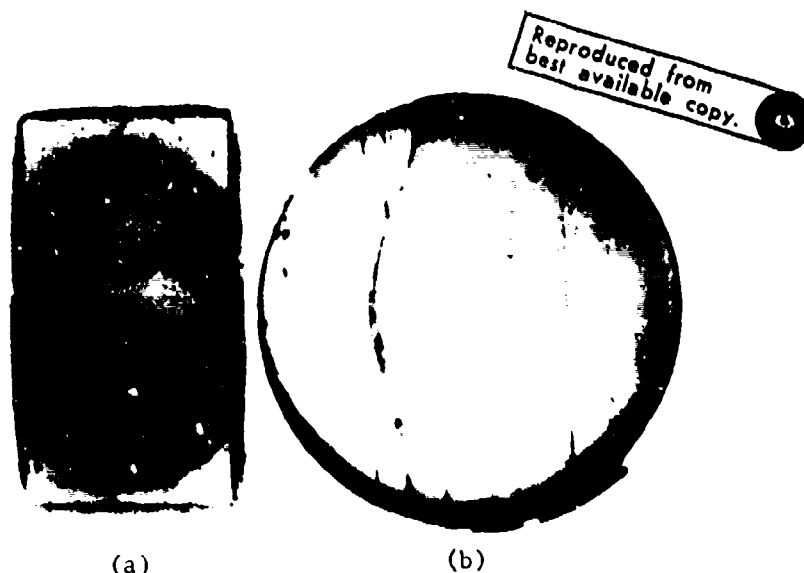(a)   (b)

Fig. 10. Relative translucency of Grace S-5570 spinel (a) hot molded
          (ODHP-12, Table 10), and (b) hot pressed in 4.6 in. dia,
          200 tons @ 2300°F for 60 min (NB-1-194[29]). Back lighted.

(ODHP-3/4, 5, 6, and 11) were accidentally ruined during grinding on a
Blanchard machine during finishing at Kodak.[28] These whole blanks were
crushed, released from the work holder, and broken into many pieces.

Hot Pressing Grace S-5570 Spinel

Since an insufficient quantity of comparable material from Phase I
for fabrication of additional samples remained either at Kodak or at
the University, arrangements were made to acquire, *gratis,* a modest
quantity of Grace spinel identified at Lot S-5570. Its behavior in
preliminary pressings is described in Fig. ° and Table 10. Since this
material (unmilled) was not very amenable to hot molding, it was pro-
cessed in a large conventional refractory metal hot pressing die,
4.6 in. dia, in the final attempts to obtain one more sound 2 x 4x1/4 in.
piece. Fig. 10 compares the results of the first hot molding and hot
pressing attempts with Lot 5770 material.

Thereafter, an additional specimen identified as NB-2-197 was
successfully hot pressed under these conditions:

> Charge: 310g Lot S-5570, screened thru 100-mesh
> Cold Press: 80 tons, top and bottom carbon spacers
> Temperature-Pressure Sequence: Heat to 600°F, no load;
>   load to 200 tons, hold for 1 min, release; continue
>   heating to 2300°F, no load; load @ ~10 tons/min to
>   200 tons, maintain 200 tons @ 2300°F for 60 min; end
>   run, releasing load and heat.

The specimen was opaque and white at the periphery, but whole and
translucent within. A 2 x 4x1/4 in. blank of moderately high trans-
lucency was cut and polished, which, with ODHP-7, -8, -9, and -10,

Table 10. Summary of Hot Molded 2 x 4 x 1/4 in. Specimens

Identity	Charge	Pretreat	Pressure-Temperature Sequence	Bulk Density	Comments
ODHP-1[26]	185g(T-1)	Coldpress @ 10,000 psi; heat to 1850°F no load	10 tons @ 1850°F, building to 75 tons @ 2200°F in ~1 hr, increase to 100 tons in ~20 min., cool to 2000°F at 100 tons, increase to 115 tons @ 2000°F for 5 min; end run, releasing load and heat	not determined	Central portions translucent, red; outer sections opaque. Broken due to sticking to mold parts.
ODHP-2[26]	185g(T-2)	Coldpress @ 10,000 psi; heat to 2000°F no load	Load slowly to 115 tons @ 2000°F, while still heating; maintain 115 tons @ 2200°F for 30 min., end run, releasing load and heat.	not determined	Corners and periphery opaque, central area translucent, red. Broken due to sticking, less severely than ODHP-1.
ODHP-3[26]	185g(T-1)	Coldpress @ 10,000 psi; heat to 1750°F no load; graphite cloth parting layers top & bottom	Load slowly to 115 tons @ ~1750° (still heating); run aborted @ ~2100°F and 75 tons due to power failure.	est. 80 - 85% of ρ_{th}	Sample whole, white, opaque. Repressed - see ODHP-4.
ODHP-4[26]	Partly densified blank no load from ODHP-3; graphite cloth parting layers	Heat to 1750° no load	Load @ ~5 ton/min to 115 tons (still heating), maintain 115 tons @ 2200°F for 30 min.; and run, releasing load and heat.	3.366 g/cm³ (~93.9%)	Sample whole. 1 1/2 x 3 in. central area translucent, red; remainder, white, opaque.

Sample	Charge	Process	Pressing	Density	Observations
ODHP-5 [26]	185g(T-2)	Coldpress @ 20,000 psi; presintered in air at 1100°C, 2 hr. Heated to 1750°F, no load; graphite cloth parting layers top and bottom	Load @ ~5 ton/min to 115 tons (still heating), maintain 115 tons @ 2300°F for 30 min.; end run, releasing load and heat.	3.379 g/cm^3 (~94.28%)	Sample whole. 2 1/2 x 3 1/4 in. central area translucent, red; remainder grey-white, opaque.
ODHP-6 [26]	185g(T-2, T-3)	Coldpress @ 20,000 psi; sintered in air @1100°C, 16 hr. Heated to 1750°F, no load; graphite cloth parting layer top and bottom	Load @ ~5 ton/min to 115 tons (still heating), maintain 115 tons @ 2300°F for 30 min.; end run, releasing load and heat.	3.427 g/cm^2 (~95.6%)	Sample whole. 2 1/4 x 3 1/8 in. central area translucent, red; remainder, corners opaque.
ODHP-7 [26]	185g(T-3)	Coldpress @ 20,000 psi; Heat to 2300°F no load; graphite cloth parting layer top and bottom. Hold @ 2300°F (~1260°C) for 2 hr (in vacuo), cool to 1700°F for 5 min.	Start heating again @ 1700°F, load @ ~5 ton/min to 115 tons; maintain 115 tons @ 2300°F for 30 min.; end run, releasing load and heat.	3.497 g/cm^3 (~97.5%)	Sample whole, but showing healed cracks. Translucent central area smaller, less dark than ODHP-6.

Identity	Charge	Pretreat	Pressure-Temperature Sequence	Bulk Density	Comments
ODHP-8 [26]	185g(T-3)	Coldpress @ 20,000 psi; sintered in air @ 1200°C, 4 hr. Heated to 1700°F, no load; graphite cloth layer top and bottom	Load @ ~5 ton/min to 115 tons (still heating); maintain 115 tons @ 2300°F for 30 min.; end run.	3.523 g/cm³ (~98.31%)	Sample whole, no open or healed cracks. 1 3/4 x 2 3/4 in. Central area more translucent, darker coloration than ODHP-7, Flowed and filled mold better than #7, but not as well as #6.
ODHP-9 [27]	185g(T-3)	Coldpress @ 20,000 psi (~37% of ρ_{th}); Heat to 2150°F, no load; graphite cloth top and bottom	Load @ ~5 ton/min to 115 tons (still heating); maintain 115 tons @ 2300°F for 1 hr; end run, releasing load and heat.	3.513 g/cm³ (~98.02%)	Sample whole except for slight open crack at edge. Central area not as large or translucent as ODHP-5.
ODHP-10 [27]	185g(T-4)	Coldpress @ 20,000 psi; sintered in air @ 1260°C, 20 hr. Heat to 2200°F and soak 15 min., no load; graphite cloth top and bottom	Load @ ~5 ton/min to 115 tons (still heating), maintain 115 tons @ 2300°F for 1 hr; end run, releasing load and heat.	3.518 g/cm³ (~98.17%)	Sample whole. Flowed out about same as #9. Translucent and less red in central area.

ODHP-11 [27]	185g (T-4)	Coldpress @ 20,000 psi; heat to 1750°F no load; graphite cloth top and bottom	Load @ ~5 ton/min to 115 tons (still heating); maintain 115 tons @ 2300°F for 1 hr; end run, releasing load and heat.	3,406 g/cm³ (~95.03%)	Pressing flat (mold component) distorted. Sample opaque. T-4 material seems to press differently.
ODHP-12 [29]	200g Grace spinel, Lot S-5570, as received	Coldpress @ 20,000 psi (36% of ρ_{th}); no pre-sintering; heat to 2175°F no load; graphite cloth top and bottom.	Load @ ~5 ton/min to 125 tons; maintain 125 tons @ 2300°F for 1 hr; end run, releasing load and heat.	not determined	New pressing flat distorted. Several cracks noticed; ends and corners opaque, white. Remainder translucent, except for white specks, agglomerates.

(a)   (b)   (c)   (d)
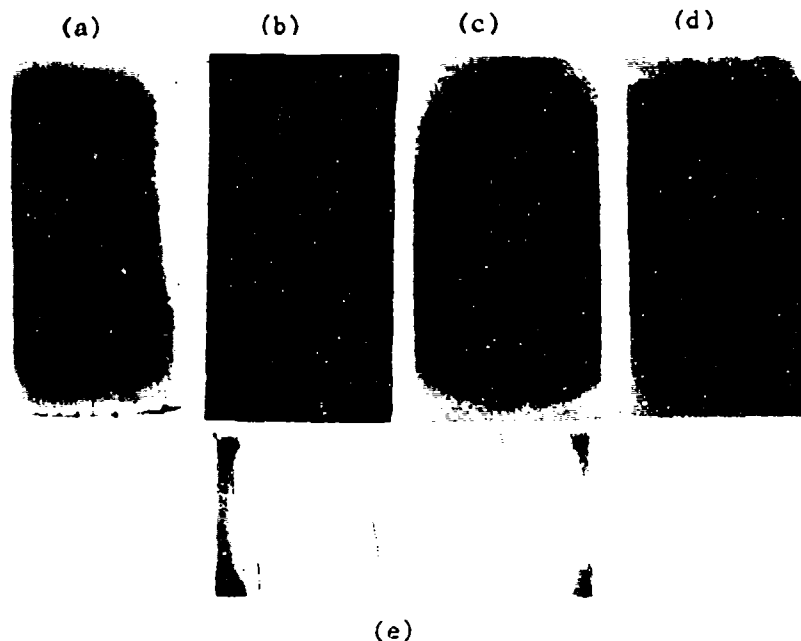
(e)

Fig. 11.   Relative translucency of five plano-plano polished 2 x 4 x 1/4 in.
           spinel pieces: (a) ODHP-7, (b) ODHP-8, (c) ODHP-9, (d)
           ODHP-10, and (e) blank cut from 4.6 in. dia hot pressing,
           NB-2-197. Specimens backlighted. Top four produced from
           sulphate-derived spinel from Phase I, reddish in color;
           bottom specimen produced from Grace spinel S-5570, trans-
           lucent, greyish in color.

completed the set of five such specimens called for in the contract.
These specimens are illustrated in Fig. 11.

Microstructures

Microstructural studies (not illustrated) have confirmed the very
gassy nature of the sulphur-laden Phase I spinel powders and the
resultant deleterious effects upon the densification process undertaken
by Kodak. Those process variations (e.g., presintering, heating to
relatively high temperatures *in vacuo* under no-load conditions, etc.)
which facilitated substantial outgassing within the open porosity
regime tended to favor densification; failure to provide for such out-
gassing resulted in opacity, associated with many microstructural
evidences of trapped branching pores, presumably gas-filled. Both
kinds of spinel, whether hot pressed or hot molded, yielded at ~2300°F
(1260°C) the rather uniform and equiaxed fine grained (~0.2μm) structure
obtained in earlier studies.[6,8,10] Specimens which were cut down and
hot pressed a second time (press-forged) retained the uniformity of
microstructure, but had somewhat larger grain size (~0.3-0.5μm). In
this case, grain growth is thought to be related to strain-anneal pro-
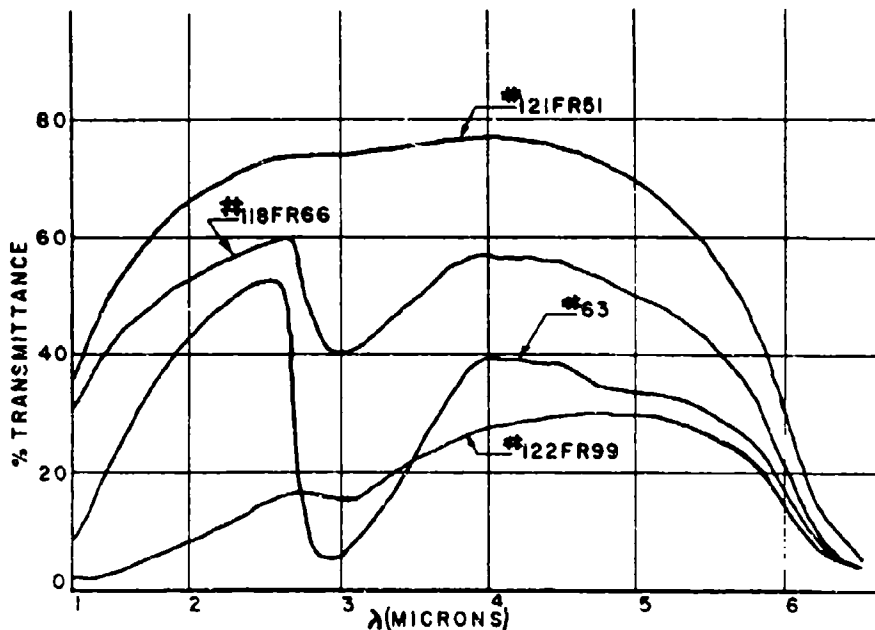cesses (additional straining, longer time at temperature), and is

Fig. 12. Infrared transmittance curves for various spinel discs hot-pressed from sulphur-derived Phase I spinel powder.[27]

associated with some improvements in translucency. The latter effect may be related to pressure- and strain-induced reductions in pore size (below optical wave lengths) as well as to time-temperature dependent (diffusional) reductions in total pore volume.

Infrared Transmission

Figure 12 shows that process-related improvements in densification and translucency are possible, even if the quality of the starting powder is not optimized. Figure 13 gives comparative data for two specimens fabricated from the Grace S-5570 spinel. Comparisons of Figs. 12 and 13 suggest that absorption bands in the infrared may be characteristic of the anions of the respective precursors and perhaps other impurities.

Phase IIB: Rate Controlled Sintering of Spinel

The findings of this phase of the study have been reported in detail in a recent dissertation,[23a] from which the text of this section largely has been taken. This work has now been presented orally,[23b] and the material is being readied for submission as two separate papers
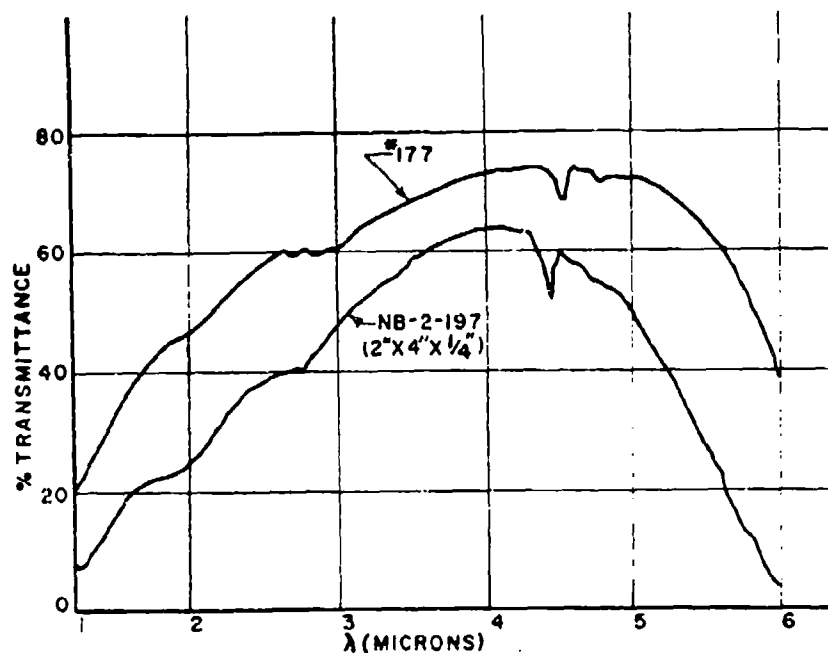
Fig. 13. Infrared transmittance curves for thin (#177) and thick
(NB-2-197) spinel pieces hot pressed from Grace S-5570
spinel powder.[29]

intended for _Journal_ publication. Details of the work,[23a] were for-
warded to AMMRC and a summary is given here.

1. Finely divided, magnesia-rich magnesium aluminate spinel
   (Grace S-2 DBM, Table 2), cold pressed to 50 percent density,
   was sintered under conditions of programmed rates of densi-
   fication (rate controlled sintering).
2. Constant densification rates ranging from 2.85×10^{-4} min^{-1}
   to 6.19×10^{-3} min^{-1} were successfully maintained during these
   experiments.
3. For the sintering of spinel at constant densification rates
   between 60 and 90 percent of theoretical density a rate in-
   dependent correspondence of temperature and density was
   discovered:

$$lnD = 1.96 + 1.48 \times 10^{-3}T.$$

4. For rate controlled sintering of spinel between 60 and 90 per-
   cent of theoretical density, the maintenance of constant
   densification rates resulted in constant heating rates:

$$\frac{dD}{Ddt} = 1.48 \times 10^{-3} \frac{dT}{dt}.$$

5. A microstructure consisting of idiomorphic, cubic grains[32] was formed in spinel samples that were subjected to the following treatments:
   a. Heating of powder compacts at 4.0°C/min to temperatures ranging from 1225°C to 1392°C (resulting in densities ranging from 66 to 86 percent of theoretical);
   b. Rapidly cooling to room temperature;
   c. Reheating at 4°C/min to 1225°C, followed by 0.162°C/min from 1225°C to 1485°C (resulting in a final density of 94 percent).

6. The kinetic data from experiments in which spinel powders were sintered at constant densification rates were observed to be non-Arrhenian, and were interpreted to indicate that the sintering process is not diffusion controlled; rather, they suggest that the principal mass transport mechanism is plastic flow.

7. The isothermal densification rates of spinel samples, having been previously sintered at varying constant rates to ~94 percent density and later reheated to 1420°C, decreased with increasing values of prior constant densification rate. Prior densification rates $\geq$ 17 x 10^{-4}min^{-1} (equivalent to ~1.1°C/min) resulted in negative isothermal rates (i.e., bloating), as shown in Fig. 14.

For reasons already described, it was not possible within this program to extend this phase of the work experimentally beyond Johnson's controlled linear densification rate range, reaching fractional densities of ~94 - 95%. To achieve transparency, ultimately one must go well into final stage densification, >>99%.

The final stage of densification in spinel for fractional densities above 93 - 95% must involve the removal of closed pores by diffusional processes. There is much kinetic and microstructural evidence that closed pores in this material contain gas phases entrapped during earlier stages of densification. The very plastic nature of spinel in this temperature range (> 1400°C) clearly contributes to its very marked tendency to bloat under very modest temperature increases. Although densification during the intermediate stage is essentially independent of densification rates during that stage, the final stages of densification are quite sensitive to rates which obtained during the intermediate stage (see Fig. 14), probably as a consequence of greater quantities of gas which had been trapped in branching pores at the faster densification rates. Intuitively, one reasons that outward diffusion of the gaseous species (under conditions involving very gradual heating to avoid unnecessary bloating of the ductile matrix) will be the key to successful final stage densification in this material. The ductile behavior of spinel at high temperatures involves very mobile dislocations moving on multiple slip systems. This degree of plasticity is not common in most ceramic materials, and hence effects associated with ductility may be relatively unfamiliar to many ceramists concerned with densification. The bloating effects described here are sensitive not only to the increased pressure of the trapped gas phase associated with any incremental
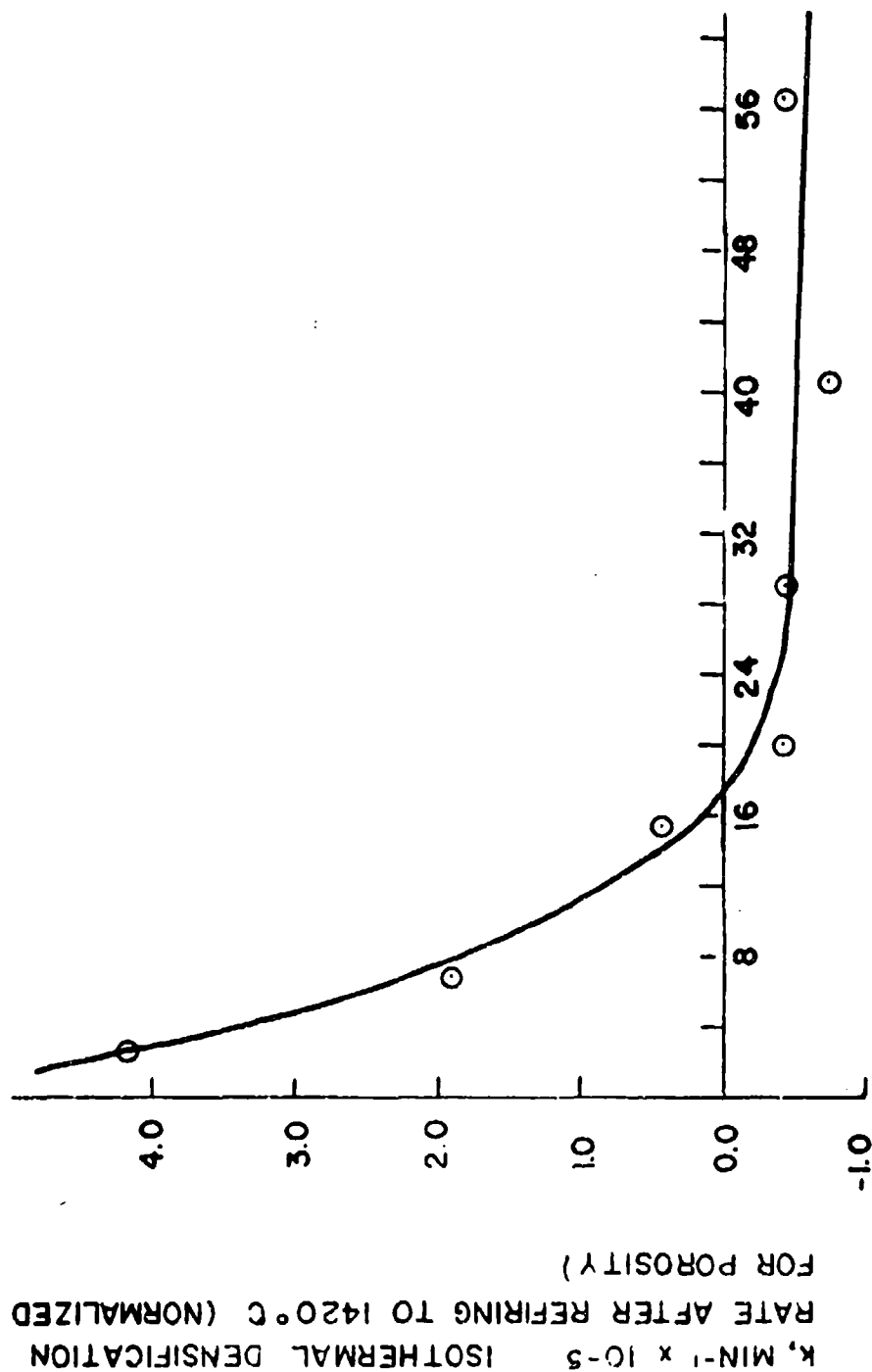
Fig. 14. Isothermal densification rate as a function of prior constant densification rate in initial stage sintering of spinel. (After Ref. 23).

temperature advance, but in particular, are responsive to the marked influence of an upward change in temperature upon the mobility of pre-viously work hardened dislocations in the surrounding crystalline mate-rial. With fast rates at high temperatures, gross bloating not only can but almost certainly will occur. High temperature, long time final stage sintering treatments being employed for spinel by other investi-gators are likely to have been needed primarily to compensate for gross bloating which almost certainly had been "built-in" during earlier ra-pid shrinkage occurring at temperatures well into the ductile range.[33]

Rate controlled sintering optimized for final stage densification, not just for linear rates, has not been achieved to date. Though not yet specifically developed for efficient densification of spinel as it now has been for alumina[24], this still novel approach continues to be an attractive one. While it may not directly achieve transparency *per se*, rate controlled sintering may prove to be effective in prepar-ing well outgassed, nearly dense compacts (intermediates) well suited for subsequent final stage densification to transparency by controlled atmosphere sintering, hot pressing, or press-forging.

SUMMARY AND CONCLUSIONS

In terms of direct results, that part of this effort aimed at producing
transparent polycrystalline spinel shapes did not turn out as well as one
might have expected from prior (small-batch) work. The technical problems
encountered are common ones in scale-up campaigns; individually, they tend
to be amenable to relatively straightforward identification and correction,
but collectively and in conjunction with other operational factors, they
can and do result in cascade effects of considerable magnitude. In this
case, the process for powder production in Phase I was not brought under
adequate chemical control for a variety of reasons, none of which were
really apparent at the time the material was being produced. Thereafter,
lack of good material created unexpected difficulties for the hot molding
effort in Phase IIA, effectively preventing meaningful optimizations of
optical properties. Similarly, "critical experiments" capable of demon-
strating final stage densification by rate controlled sintering, based on
valuable nonisothermal kinetic information which had been gained in
Phase IIB, were adversely affected. Yet many important and positive things
have been learned, and described herein, which ultimately should be of
value in scaling up production of high quality spinel materials from any
precursor, and in subsequent densification processes suited to production
of large transparent shapes.

In retrospect, it would have been most desirable (and in the future
should be considered mandatory in programs of this nature) to assure
that timely, local access to reliable analytical services be routinely
available for on-line process control as well as for *post facto* quality
assurance. This viewpoint certainly implies no disparagement of the
analytical services provided most cooperatively by the vendor involved.
Rather, it acknowledges that the process-analysis-control linkage is so
intimate and so demanding of promptness that it cannot be managed effectively
at a distance.

More emphasis should have been placed upon dynamic processing of
the precursor salt, in the interests of developing a very uniform and
reproducible feed material for the dynamic calcining furnace. For
example, continuous casting of a relatively thin sheet (~1/16 in. thick)
would have permitted more rapid cocrystallization, better drying, easier
comminution, and a more uniformly sized feed material for the furnace,
as well as more efficient handling and consequent minimization of expo-
sure to contamination.

Though optimization of sulphur removal was not achieved in these
experiments, the dynamic calcining furnace worked quite well, and is con-
sidered to offer considerable promise for efficient and reproducible
processing of reactive ceramic powders. [This view has been confirmed by
more recent work, done elsewhere[34]]. It is, however, very dependent upon
close control of feed material (constitution, size, and size distribution)
if a uniformly fired product is to be produced.

It is probable that sulphur is "a bad actor" where spinel is concerned,
and that, hereafter, spinel derived from precursors other than sulphates should
be emphasized. There are a number of unresolved scientific questions about the

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physiochemical form of sulphur residues in spinel powders, and about
the characteristic reddish color developed when such powders are den-
sified at high pressures by hot pressing and/or hot molding. When re-
heated at temperatures above that at which they were densified, many
ceramics hot pressed to transparency tend to bloat and become opaque.
Sulphur-derived spinel follows this pattern[8]. Recent unpublished re-
search, comparing direct transmission electron microscope images ob-
tained from ion beam thinned foils of unbloated and bloated spinel,
indicates that the bloating begins on an almost molecular scale in
otherwise homogeneous grains, tending to cluster in very tiny bubbles
rather reminiscent of fission fragment gases clustering in irradiated
nuclear fuel materials. The implication is that the sulphur residue,
SO_x, may have been accomodated directly within the spinel structure
itself. If so, this may explain the tenacity with which spinel powders
retain sulphur during calcination, even at temperatures well above the
dissociation points of its precursor salts.

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